

PATENT
0595-1030

IN THE U.S. PATENT AND TRADEMARK OFFICE

In re application of

Patrick BOSCHET et al. Conf. 1820

Application No. 10/533,446 Group 1791

Filed May 2, 2005 Examiner J. Wollschlager

STRIPPING PRODUCT FOR COATING A MOULD FOR MAKING A COMPOSITE
MATERIAL PART

DECLARATION UNDER RULE 132

Commissioner for Patents
P.O. Box 1450
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October 5, 2009

Sir:

I, Dr Patrick NOIREAUX, hereby declare as follows:

My relevant background is as follows:

I, Dr Patrick NOIREAUX, am a graduated Engineer in Research and Development, at the Materials Department in the Centre of Transfer of Technology of le Mans (CTTM), located 20 rue Thales de Milet, 72000 Le Mans, France (<http://www.cttm-lemans.fr>).

I hold an University Thesis in organic chemistry at the University du Maine (Le Mans, France) and was graduated in June, 1973 (Thesis Title: Chemical modification of polyenes by use of chlorosulfonyl isocyanate - model molecules).

The main professional functions I occupied are: Research assistant at IMM (1973-1976); Research Assistant at the Institute of Research in Applied Polymers (IRAP 1976-1994); Research and Development Engineer (IRAP 1976-1988); Project manager (IRAP 1988-1992); Head, adhesives and bonding group (CTTM 1994-present); Head, radiations/surface/polymers group (CTTM 2005-present).

I also work Materials Expert, with Main topics of research: UV curing and formulation (varnish, ink, paint, adhesive, (IRAP 1976-1980); chemistry of organosilicon compounds (IRAP 1984-1994); polysiloxane, primers for bonding elastomers to metal or composite (IRAP 1980-1984); polysilane, precursor of ceramic -silicon carbide (IRAP 1984-1988); polysilane, thermostable matrix crosslinked by ionising radiation for composite material (IRAP - CTTM 1989-1994); development of a radiation platform -Corona, cold plasma, UV, EB- (CTTM 1994-2005); Fire and heat resistant polymers (CTTM 2005 - 2008).

I occupied other professional functions: Collaboration with university: support to post Master students (thesis, DEA, DESS levels); Short-term Professor at the Institute of Superior Mechanicals and Materials Advanced (ISMANS - engineer school, organ silicon chemistry); Organization of congresses.

Besides, I would like to point out that I have already been involved in numerous patent applications, as per in the US patent application 09/008,742 that was granted as US 5 993 918

for a "Thermo bonding interlining with dots of thermo fusible polymer via electron bombardment and process for making the same".

I have read the Official Action mailed April 28, 2009, and I have reviewed the pending claims and the present application.

It appears that the Official Action does not appreciate the unexpected superior results obtained with the claimed stripping composition, which has been coated onto a mold for making a composite material part with the claimed stripping composition.

Among these unexpected superior results, one should point out that although the stripping composition according to the invention is claimed and described (finally) only for a molded composite part for which the curing step is made by thermal action (e.g. heating via resisting or inductive systems in the mould structure), the base ingredient, the polymerization agent, the anti-adhesion modulator and the two major components of the anti-stick agent are all industrial products initially dedicated to the UV curing of polymers.

This is certainly one of the reasons why the prior art of record is mentioning some chemical families that may seem quite resembling to the features of the invention.

However, the new main claims have been amended to mention that the composite part obtained with the stripping product of the invention is polymerized by heating.

Now, explanation of the major failings of the prior art is exposed, in view of the specification of the application (see e.g. in US 2006 255 509 A1 at [0003] and [0023] to [0028]).

First of all, the prior art products are "tacky prior to polymerization" as understood from [0009] in US 2006 255 509 A1.

In the professional language of polymers chemistry, the products are divided according to their viscosity.

Should a product be liquid, it is called as belonging to "stage A" viscosity category. Typically, so called "linear" products, i.e. non reticulated products belong to "stage A" category and are considered as "liquids". They mostly comprise linear atomic links kind of "in 2D" network structure.

For instance, both the stripping composition and the specific "anti-adhesion modulator" of the invention are "stage A" products (See for instance in US 2006 255 509 [0031]: "The stripping composition of the invention is liquid").

As of the stripping composition according to the invention, the measurement of the viscosity as per the specification ECA3076 at a temperature of 25°C, is of: 130 +/- 20

mPa.s. This measurement of the viscosity was made under the following conditions: viscometer - rheometer with a conical geometry / plane: C35 / 1°; diameter of 35mm; air-gap = 0,052 mm; Volume 0,2mL; Dynamics 20 a 40°C; Velocity: 2°C/min; Constraint 100Pa.

Such a viscosity of the stripping product of the invention is specifically efficient for the unmolding of composite parts of quite a big size, such as helicopter rotor blades.

Such a viscosity must be low enough to, on the one hand allow a fast, thin and regular application, thus avoiding waste and lost of time.

On the other hand, this stripping composition must adhere correctly the mould in a perennial manner, even upon the inner vertical portions of the cavity of the mould. With the invention, the anti-adhesion modulator is made of a silicone polymer. This modulator is constituted by a polydimethylsiloxane (PDMS), having the form of a linear (non reticulated) epoxy function.

The datasheet of the example of industrial anti-adhesion modulator exposed in the specification (See for instance in US 2006 255 509 [0011]: "UV RCA 200") is enclosed to illustrate the category of product to be used.

However, when the application was filed, this product was made by the late Chemical firm RHODIA. This firm is now

incorporated into the Group BLUE STAR SILICONES. The datasheet is therefore available from www.bluestarsilicones.com, as Technical Data Sheet n° SIL 97 221 3 - June 1997: "SILCOLEASE® UV RCA 200".

Unlike the invention, the semi reticulated polymer compounds are designed to be "tacky", when they belong to "stage B", since they comprise atomic links "in 3D" between Si, O and CH₂ elements.

Most of the polydimethylsiloxane (PDMS) mentioned in the prior art are therefore producing "tacky" (not liquid) compounds.

So as to obtain a final product from such "tacky" or "stage B" semi reticulated polymer compounds, the general knowledge in the polymer chemical industry is systematically recurring to the heavy adding of diluents / solvents (see e.g. US 5 650 453, column 6, lines 31-35 and 40-45).

This leads to the prior art drawback of producing and handling polymer including dumping volatile organic compounds, e.g. diluents.

Such compounds are quite dangerous for people in the vicinity, for instance to those in charge of applying the stripping composition inside the molds in view of making helicopter composite blades.

Furthermore, in order to be either environment friendly and / or to cope with regulations, such dumping volatile organic compounds, e.g. diluents, are more and more to be avoided in the industry.

As explained hereinabove, the general knowledge in the polymer chemical industry is systematically providing for the adding of diluents / solvents (e.g. see US 5 650 453, column 6, lines 31-35 and 40-45).

Finally, the use of diluents / solvents has been revealed by the laboratory and industrial use of the invention, to be obliging to apply excessive quantities of stripping product.

Oppositely, the general knowledge in the art of applicable polymer compounds, usually considered that on the one hand, applicable polymer compounds using diluents / solvents was the best known solution to have the minimum quantity of such a compound applied.

On the other hand, such a minimum quantity of applied compound also provides for a limitation of the polluting remains that finally stay into the cavity of the mold.

Thus, with the invention, it is possible to use the mold a plurality of times with one single applying of stripping product. With the same moulds and in molding conditions, before

the use of the stripping product according to the invention, it was generally compulsory to clean the mold before every molding.

So as to illustrate the above, the following chart exposes how many helicopter rotor blades have been molded within two standard molds (#1 & #2), and how many applications of stripping product are required for each series of molded parts:

MOLD TYPE (#)	COMPOSITE PART TYPE	QUANTITY OF MOULDED PARTS (Q)	NUMBER OF STRIPPING PRODUCT APPLICATIONS	NUMBER OF DEFECTIVE PARTS
#1	ROTOR BLADE	50	4/50	0/50
#2	ROTOR BLADE	25	1/25	0/25

At present, about 1.800 rotor blades are molded every year with the stripping product according to the invention.

With the first test (mold #1), for each series of 50 rotor blades that was molded, only four applications of stripping product was required.

With the second test (mold #2), for each series of 25 rotor blades that was molded, only one application of stripping product was required. With the stripping product used before the invention, about ten (10) applications inside the mold were necessary.

Since the stripping product of the invention is "solvent free", it was safer & environment friendly to make the applications by the people in charge of the molding operation.

Besides, it was measured that each application of stripping product only required 10 grams of product (e.g.: with one tissue impregnated with 10 grams of stripping product for each application).

While the claimed composite material is, at present, mostly used for molding rotor blades for rotary wings aircrafts, although it could be used to mold other types of composite items.

For most of these composite molded items, the molding process requires that a "high temperature" be maintained in the mould, and, thus, induces a thermal treating of the composite item.

Such a "high temperature" heating is about 100°C to 150°C, since the composite material to be molded with the help of the stripping product as per the invention is made of epoxy resins of the lower -thermal- class, i.e. withstanding temperatures below 180°C (see specification in the published application US 2006 255 509 A1 at [0029], [0030] and [0033]).

For instance, the following temperatures and molding durations are employed with the invention.

For making a standard composite rotor blade in a metal mould, a standard process cycle has a general duration of 1 hour, and a temperature of about 150°C is reached with successive steps of 25°C.

For making another type of composite rotor blade, from a thermo hardening resin in the 120°C class, in a metal mould, a usual process cycle has:

- a minimum duration of 30 minutes, with a maximum temperature of about 120°C which is reached with successive steps of about 25°C;
- an average duration of 1 hour, with a maximum temperature of about 140°C which is reached with successive steps of about 25°C;

For making another type of composite rotor blade, from a thermo hardening resin in the 180°C class, in a metal mould, a usual process cycle has:

- an average duration of 1 hour, with a maximum temperature of about 190°C which is reached with successive steps of about 25°C.

This stripping composition is perfectly adapted to the range of pressures that are applied inside the moulds during the making of the rotor blades, e.g. from 72.5 PSI to 290.2 PSI (5 to 20 bars).

With the stripping compositions used before the claimed invention, at such temperatures, these stripping compositions, or

releasing coatings, applied inside the mold would loose their properties.

In these conditions, when such high temperatures were required (e.g. for thermal treatment of composite items), a film made of "Thermalimide" was added before molding, between the mold where the stripping composition was applied, and the bulk composite item to be subsequently molded.

After molding, this film appeared to be mixed into the matrix of the composite items. As a result, it was difficult to separate this film from the molded composite item.

This problem occurred whether or not a solvent was included in the stripping composition.

The stripping composition of the claimed invention is solvent free.

Oppositely, the compositions obtained by Poly Addition (e.g. as per in ECKBERG U.S. 5,650,453, see for instance col. 7, line 3 "about 10 to 20 weight percent reactive diluents") are requiring important amounts of solvent so as to make more fluid the stage B ("cross link", see col. 6, line 43) initial product, i.e. the pre reticulated (3D) product with an added solvent for adjusting its viscosity.

For information about Poly Addition or "chain growth", see: http://en.wikipedia.org/wiki/Chain_growth_polymerisation.

Unlike the invention, the compositions as per in ECKBERG U.S. 5,650,453 is UV cured.

Similarly, the compositions obtained by Poly Condensation (e.g. as per in BRALEY U.S. 2,811,408, see for instance col. 2, line 42-44 "essential siloxane ... constitute at least 10% by weight of the mixture") are requiring important amounts of solvent so as to make more fluid the highly linked Q resin initial product, i.e. the pre reticulated (3D) product with a solvent for adjusting its viscosity.

For information about Poly condensation, see:
http://en.wikipedia.org/wiki/Condensation_polymer .

While being solvent free, the stripping composition of the invention is however very stable and is resistant to such high molding temperatures, without a loss of its specific properties during the whole molding process.

According to the specification (see the published application US 2006 255 509 A1 at [0006-0011]), the invention provides for:

- 100 parts by weight of a base ingredient consisting in a first polydimethylsiloxane (PDMS), for instance the product called UV POLY 200.

The datasheet of this example of base ingredient UV POLY 200 is enclosed to illustrate the difference of this base ingredient possibly used, with the anti-adhesion modulator.

The anti-adhesion modulator is belonging to the same overall chemical family and is also made by the Chemical Group BLUE STAR SILICONES (formerly RHODIA). This datasheet is also available from www.bluestarsilicones.com, as Technical Data Sheet n° SIL 03 153 3 – August 2003 for "SILCOLEASE UV POLY 200".

According to the specification (see the published application US 2006 255 509 A1 at [0007-0011]), the invention provides for:

– 0.5 to 10 parts by weight of a polymerization agent constituted by a diaryliodonium salt, for instance the product called UV CATA 21.

The datasheet of this example of polymerization agent UV CATA 21 is enclosed to illustrate the composition of this polymerization agent possibly used. This polymerization agent UV CATA 21 is made by the Chemical Group BLUE STAR SILICONES (formerly RHODIA). This datasheet is also available from www.bluestarsilicones.com, as Technical Data Sheet n° SIL 98 060 3 – March 1998 for "SILCOLEASE® UV CATA 211".

According to the invention, the stripping composition also comprises an anti-stick agent including:

- 8 to 12 parts by weight of dodécylo mono vinyl ether (DDVE), for instance produced by SIGMA-ALDRICH (see: <http://www.sigma-aldrich.com>) with the Compound ID 69826 (or 413496_ALDRICH).
- 8 to 12 parts by weight of cyclo hexane dimethanol divinyl ether (CHVE), for instance produced by SIGMA-ALDRICH with the Compound ID 3437285 (or 416171_ALDRICH).

For both these dodecyl mono vinyl ether (DDVE) and cyclohexane dimethanol divinyl ether (CHVE), datasheets are enclosed, as available from: <http://pubchem.ncbi.nlm.nih.gov>).

The references cited in the Official Action fail to suggest the superior results of the claimed invention.

ECKBERG U.S. 5,650,453 is proposing an UV curable composition, which has to be heavily added with a solvent in order to reach a convenient fluidity. Therefore, this composition cannot be considered as "solvent free liquid" as the stripping composition of the invention.

Besides, the composition of ECKBERG U.S. 5,650,453 is of stage B type (pre reticulated) obtained by Poly Addition or Chain growth polymerization, while the invention is of a

different chemical production type, i.e. makes use of a smart modulator able to provoke the reticulation only when the stripping composition is "in situ" (in the heated mold).

Without the addition of solvent, such a composition as per ECKBERG U.S. 5,650,453 is "tacky".

Furthermore, ECKBERG U.S. 5,650,453 explicitly excludes the combination of its teaching with the teaching of BRALEY U.S. 2,811,408 which is describing a Q type resin obtained by Poly condensation.

ECKBERG U.S. 5,650,453, for example, is directed to a low viscosity composition for covering various products. There is no suggestion of utilizing a stripping composition that is suitable for high technology, thermally curable, molded composite items. ECKBERG U.S. 5,650,453 is limited to much lower maximum molding temperatures, e.g., maximum 100°C or 115°C.

Unlike BRALEY U.S. 2,811,408 are proposed by ECKBERG U.S. 5,650,453 poly siloxane with epoxyde groups, the adding of vinyl ether, and a catalysis agent of the Ionium type (thus making the curing compulsory with either UV or EB technique). So as to make soluble the catalysis agent of the Ionium type, great amounts of vinyl ether (more than 20 %) are described.

As exposed, BRALEY U.S. 2,811,408 proposes a highly linked Q resin initial product, i.e. the pre reticulated (3D)

product including a solvent for adjusting its viscosity. This composition aims to be applied to foam molded products, not to the making of composite parts such as rotor blades for helicopters.

It is well known from the man of the art that Q resins including Si-O linking are difficult to make soluble with CH₂-CH₂ pre reticulated polysiloxane (as in ECKBERG U.S. 5,650,453).

In the composition of BRALEY U.S. 2,811,408, there is no provision for a polydimethylsiloxane (PDMS), since there is no linked Si-H or vinyl. The Q resin as per BRALEY U.S. 2,811,408 is of organo polysiloxane and does not provides for an epoxy function (see e.g. Col 4, example 4).

It is clear that BRALEY U.S. 2,811,408 does not describes or suggests a solvent free liquid, with an epoxy polydimethylsiloxane(PDMS) as a base ingredient, and with another polydimethylsiloxane(PDMS) as a anti-adhesion modulator, i.e. a linear silicone polymer with an epoxy function.

Besides, the man of the art perfectly knows that condensing the siloxane compounds so as to obtain a Q resin is a process which is very hard to industrially conduct. Should an epoxy function be used, it is known that this would provoke a composition which is altering the surface aspect of the molded part.

The poly condensation process of BRALEY U.S. 2,811,408 (filed in 1954) is not compatible with the poly addition process

of ECKBERG U.S. 5,650,453, while the latter being filed more than 40 years later: should the combination of these two teachings have been either obvious or helpful, the man of the art would certainly have embodied it.

ECKBERG U.S. 4,256,870 proposes a composition which is obtained by poly addition, and that leads to a pre stage B product. The aim is to make the pot-life of the composition which is longer. For the RTV catalysis, a platinum (Pt) based component is added.

Obviously, ECKBERG U.S. 4,256,870 does not describes or suggests a liquid without methyl hydrogen cross linking agent, with an epoxy polydimethylsiloxane(PDMS) as a base ingredient, and with another polydimethylsiloxane(PDMS) as a anti-adhesion modulator, i.e. a linear silicone polymer with an epoxy function.

LOPES U.S. 4,681,714 is limited to a solvent-containing stripping composition for use at low molding temperatures.

LOPES U.S. 4,681,714 proposes a poly condensation coating having a convenient inertia when in contact with PU foams. This composition is obtained by a poly condensation chemistry process. Since this composition is solvent containing, no combination with ECKBERG U.S. 4,256,870 or ECKBERG U.S. 5,650,453 would approach the invention. Similarly, the invention

couldn't be extracted from a attempt to combine LOPES U.S. 4,681,714 with BRALEY U.S. 2,811,408.

DMITROFF U.S. 3,321,019 teaches molded helicopter blades, made from fiber glass.

Thus, based on the teachings of the cited references there is no suggestion that the claimed stripping composition would be capable of providing a very stable release material, without a loss of its specific properties during the whole molding process.

Another important advantage provided by the invention, is useful when the composite part which is molded has to be painted after its making (see e.g. in US 2006 255 509 A1 at [0022]) and when a high quality surface aspect is required.

The man in the art is perfectly aware that the presence of siloxane compound on the outer surface of a molded object, is a very frequent source of poor quality in surface aspect and painting. Usually, it is compulsory with such siloxane compound on the outer surface of a molded object, to provide for a special treatment, before the painting is applied to this object.

Surprisingly, the invention allows for the painting to be applied directly after molding, with no special treatment.

The undersigned declare further that all statements made herein of their own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under §1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dr Patrick NOIREAUX, Graduated Engineer in Research and Development, Materials Department, CTTM, France.

Date: Friday, 23 October 2009

Enclosures:

- Datasheet of BLUE STAR SILCOLEASE® UV RCA 200.
- Datasheet of Datasheet of BLUE STAR SILCOLEASE® UV POLY 200.
- Datasheet of BLUE STAR SILCOLEASE® UV CATA 21.
- Datasheet of dodécycle mono vinyl ether (DDVE) SIGMA-ALDRICH Compound ID 69826;
- Datasheet of cyclo hexane dimethanol divinyl ether (CHVE) SIGMA-ALDRICH Compound ID 3437285.